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Dynamical Solvent Effects on Electron-Transfer Processes:

Recent Progress and Perspectives

by

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Introduction

→ The last decade has seen a remarkable upsurge of interest in the dynamical role of the solvent in liquid-state chemical processes.¹ Along with the intrinsic importance of such phenomena in chemistry and biology, these activities have been fostered by substantial recent developments of both a theoretical and experimental nature. The central concept of solvent "friction", whereby the collective solvent motion necessary to surmount the activation barrier slows the rate below that expected from transition-state theory (TST),^{1a-c} has spawned a myriad of theoretical treatments that attempt to describe the effective solvation dynamics. The ensuing interplay with experiment has considered chemical systems ranging from highly activated thermal reactions to ultrafast photoinduced processes where the solvation dynamics alone determine the reaction timescale.²

Although the range of chemical processes of significance in this context is necessarily wide, of particular interest are those involving electron or related charge transfers. For such systems, the solvent plays a pivotal role in determining the activation energetics and often also the reaction thermodynamics. Such energetic (or "static") factors, arising from the changes in solvent polarization that necessarily attend the transfer of charge, are well known; they form central aspects of the Marcus and related kinetic treatments.³ The recognition of an additional *dynamical* role of the solvent upon the charge-transfer kinetics, i.e. upon the frequency of barrier crossing, is of much more recent origin. The timescales for collective solvent dipole rotations and translations associated with progress along the reaction coordinate are known to be sensitive to the solvent structure, so that wide variations in the reaction dynamics can be anticipated.

Current experimental inquiries into solvent dynamical effects in electron

transfer are, broadly speaking, of two types. The first involves measurements of time-dependent fluorescence Stokes shifts (TDFS) for chromophores forming suitable charge-transfer excited states.^{2,4,5} Such measurements probe the real-time dynamics of polar solvent relaxation around a newly formed dipole. Recent instrumentation advances enable relaxation times down to ca 10^{-13} s to be followed.^{2b,6} In addition, measurements of electron-transfer (ET) rates themselves, either from photoexcited or ground states, can yield solvent dynamical information. Most intramolecular photoexcited ET processes examined so far in this regard yield reaction times comparable to the solvation times, τ_s , extracted from TDFS measurements, indicating the presence of only small or negligible activation barriers ($\leq k_B T$, where k_B is the Boltzmann constant).^{2b,c}

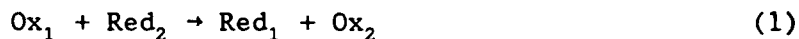
Such ultrafast TDFS and ET rate measurements provide direct information on charge-induced solvent relaxation, and have justifiably been accorded considerable attention in the recent literature.^{2,4,5} Most chemical ET processes, however, involve sizable activation barriers which can modify significantly the influence of solvent dynamics on the reaction rate. The dynamical description of such activated ET processes has attracted widespread recent theoretical attention (see e.g. refs. 7-14, and below). While perhaps less abundant, related experimental studies have begun to delineate the nature and importance of dynamical solvent effects on activated ET processes.¹⁵⁻¹⁸

The aim of this Account is to outline in straightforward terms current understanding on the manner and extent to which dynamical solvent properties can influence the kinetics of electron-transfer processes, drawing in part from recent experimental and calculational results from our laboratory. Although connections will be made to dynamical information extracted from ultrafast photoinduced processes, we focus here instead on activated reactions. While several recent reviews consider the former,^{2,4,5} there

is a dearth of transparent descriptions of the latter case. An important goal here is to demonstrate how the close interplay between theory and experimental kinetic studies along with related real-time information on solvent relaxation can yield substantial insight into the nature of dynamical factors in activated electron transfer.

Conceptual Background and Pertinent Dynamical Information

We consider here outer-sphere electron-transfer reactions having the general form



The present discussion will focus primarily on bimolecular self-exchange (i.e. symmetrical) reactions, although most arguments apply with minor modification to nonsymmetrical homogeneous and to electrochemical processes. For reactions featuring significant ET barriers, $\Delta G^* > (2-3) k_B T$, the observed bimolecular rate constant can be expressed most simply as¹⁹

$$k_{ob} = K_p \kappa_{e1} \nu_n \exp(-\Delta G^*/k_B T) \quad (2)$$

where K_p is a precursor preequilibrium constant, κ_{e1} is the electronic transmission coefficient, and ν_n is the nuclear frequency factor (s^{-1}). Any influence of solvent dynamics is contained within ν_n . In general, ν_n will be comprised of appropriately weighted dynamical contributions from each of the nuclear motions that contribute to ΔG^* . In the present context, the simplest case is where virtually the entire barrier arises from solvent reorganization, i.e. where the "inner-shell" contributions from reactant bond distortions are small. In this circumstance, $\nu_n = \tau_{eff}^{-1}$, where τ_{eff} is the effective solvent relaxation time associated with ET barrier crossing.

Of central interest is the relationship between τ_{eff} and observed solvent

relaxation times. The simplest dielectric continuum treatments^{7,8a,9a} predict that $\tau_{eff} \sim \tau_L$ for cusp-like barriers, where τ_L is the well-known longitudinal relaxation time extracted from dielectric loss spectra.²⁰ This quantity denotes the relaxation time for an isotropic dipolar fluid in response to a sudden change in charge, as will occur in ET processes. Significantly, τ_L is known to be sensitive to the solvent structure, differing by at least ca 50 fold (from ca 0.2 to 10 ps at ambient temperatures) between common "Debye" solvents; i.e. those that exhibit only one relaxation in the dielectric loss spectrum.^{15c,16d} Very crudely, τ_L correlates with the solvent viscosity in some cases, although it should be stressed that the physical origins of these quantities are quite different.²²

The physical relevance of τ_L to barrier crossings can be understood simply as follows. In ET processes, especially those featuring cusp barriers, electron tunneling can occur (essentially instantaneously) only upon the formation of a transition state featuring an intermediate, nonequilibrium, solvent polarization. In the presence of so-called dielectric friction, the collective solvent dipole reorientation necessary to traverse this intersection region of the reactant and product wells is impeded by irreversible energy dissipation from a given dipole to its surroundings (diffusive or "overdamped" motion).^{1a,8a} Consequently, the timescale required for significant net progress along the reaction coordinate can be substantially longer than for individual dipole rotation. The frequency of the latter (ω_0) is determined in part by the molecular moment of inertia and corresponds to the zero-friction (TST) limit. At energies within ca $k_B T$ of the transition state, thermal fluctuations can send the system back and forth over the barrier at frequencies close to ω_0 . Nevertheless, net progress to energies further below the transition state, so that the system is effectively trapped in the products' well, occurs on the longer

timescale associated with the overdamped solvent motion. Since τ_L refers necessarily to such *dissipative* solvent relaxation,^{21,22} it is not surprising that this quantity should provide a relevant description of the timescale for ET barrier crossing under overdamped conditions.

While there is strong experimental evidence that ν_n at least correlates with τ_L^{-1} under some conditions, several factors that have come under recent theoretical scrutiny conspire to make the anticipated influence of solvent dynamics on the reaction rate rather more involved. We now consider briefly the most important of these. Most simply, even in the dielectric continuum/Debye limit τ_L will only be a faithful description of the solvent dynamics if $\tau_L^{-1} \ll \omega_o$ ("overdamped" limit).^{8a,23} In low-friction media where $\tau_L^{-1} \geq \omega_o$ (e.g. acetonitrile), the TST limiting rate will be approached so that $\nu_n \approx \omega_o/2\pi$,^{8a} whereupon solvent friction will play no role in the reaction dynamics. Largely overdamped solvent motion (i.e. $\tau_L^{-1} < \omega_o$), however, appears to be a more common circumstance.^{15b,23}

Unlike the TST case, the overdamped barrier-crossing frequency is dependent upon both ΔG^* and the shape of the barrier top.^{8a,9c,24,25} As illustrated in Fig. 1, the latter is influenced by the electronic coupling matrix element (H_{12}), reflecting the degree of donor-acceptor orbital overlap. Roughly, one predicts that $\nu_n \propto (\Delta G^*)^{1/2}$; ν_n is generally expected to diminish as the barrier-top "roundedness" increases, i.e. as the barrier becomes less cusp-like, (i.e. solid rather than dashed profile in Fig. 1). A simple rationalization of the latter effect is that barrier recrossings, yielding a lower frequency of successful diffusive passages through the intersection region and hence a smaller ν_n , should become more prevalent as the barrier top becomes broader. For barrier shapes typical in activated ET, we anticipate ν_n to be somewhat (ca 2-5 fold) smaller than τ_L^{-1} .^{24,25}

There is considerable interest currently in the degree to which the

actual relaxation times for polar solvation (and hence τ_{eff}) may differ from τ_L , particularly as a result of "solvent molecularity" effects associated with the inevitable proximity of the reorienting solvent dipoles to the reacting solute particles.^{2,4,5} One conceptually useful approach is to treat the solvent as a hard sphere dipolar fluid using the "mean spherical approximation" (MSA). This treatment yields a distribution of solvent relaxation times, increasing from τ_L for solvent molecules distant from the solute to values closer to the Debye relaxation time τ_D ²⁰ for nearby solvent.^{8b,26} Interest in the MSA model has been heightened by the observation of TDFS solvation times, τ_s , that are somewhat longer than τ_L along with multi-exponential behavior (i.e. presence of multiple τ_s values), thereby in qualitative accordance with the theoretical predictions.^{6,27} The MSA model, however, appears to overestimate the extent of these noncontinuum effects;^{2a,27-29} τ_s values measured recently for a number of polar Debye-like solvents at ambient temperatures are mostly only ca 1.5-2 fold longer than τ_L (vide infra).^{2a}

In addition to such longer τ_s components, dynamical contributions having relaxation times shorter than τ_L are often anticipated. Additional dispersions at higher frequencies in the dielectric loss spectra ("non-Debye" effects) are not uncommon (e.g. for alcohols³⁰), indicating that faster relaxation components of the solvation dynamics can be expected even in the dielectric continuum limit. Some theoretical treatments have considered solvation dynamics in terms of wavevector(k)-dependent dielectric properties, thereby including shorter-range solvation effects arising from local field inhomogeneity.^{31,32} These treatments predict the appearance of τ_s components shorter than τ_L even in Debye-like media. Although the observation of such faster relaxation components in TDFS measurements is limited by laser pulsewidth and other considerations, experimental evidence supporting their

common presence is emerging from subpicosecond studies using Coumarin probes by Barbara et al.^{2b,6}

A key issue for activated ET processes is the extent to which such faster versus slower relaxation components determine τ_{eff} and hence the overall barrier-crossing frequency.³³ A theoretical treatment due to Hynes^{9c} predicts that the faster time component(s) of dielectric loss spectra tend to provide important contributions to τ_{eff} even for relatively small-amplitude relaxations.²⁵ Other^{34,35}, but not all¹², treatments yield comparable results.²⁵ Recent numerical simulations have confirmed the basic validity of Hynes' conclusions, at least for cusp-like barriers.³⁶ An experimental test is considered below. Such treatments can also be applied to the analysis of multiple relaxation times (or distributions thereof) arising from solvent molecularity effects.³⁷

For reactions where ΔG^* contains a substantial component associated with reactant bond distortions, such motions can provide significant accelerating contributions to ν_n above that expected from overdamped solvent motion alone.¹⁰ This is because the presence of a separate inner-shell reaction coordinate, associated typically with relatively rapid underdamped motion, can provide facile additional channels for barrier passage once the system has reached the vicinity of the intersection region. Nevertheless, numerical calculations predict that slower overdamped solvent motion can typically contribute importantly to ν_n even for barriers composed of comparable solvent and inner-shell contributions.^{10b} Some experimental data is roughly in accord with this prediction.^{15d}

It is important to recognize that nuclear dynamics will control entirely the barrier-crossing frequency only if the donor-acceptor electronic coupling is sufficiently strong so that "reaction adiabaticity" is essentially achieved, i.e., when $\kappa_{e1} \rightarrow 1$ [Eq(2)]. Physically, this implies that the

splitting between the upper and lower potential-energy surfaces in the intersection region, equal to twice the electronic coupling matrix element H_{12} (Fig. 1), is sufficiently large so that the system remains on the lower surface during its passage through the transition state. If H_{12} is small, on the other hand (Fig. 1, dashed curves), the system is liable to traverse the intersection region by remaining on the reactant potential-energy surface, so that the probability of crossing to the product surface by electron tunneling is small (i.e. $\kappa_{e1} \ll 1$).

An illustrative, albeit simplified, Landau-Zener expression for κ_{e1} is^{19a,24a}

$$\kappa_{e1} = \frac{2 [1 - \exp(-\nu_{e1}/2\nu_n)]}{2 - \exp(-\nu_{e1}/2\nu_n)} \quad (3)$$

The "electronic frequency factor" ν_{e1} is given by

$$\nu_{e1} = H_{12}^2 (\pi^3 / \Delta G^* h^2 k_B T)^{1/2} \quad (3a)$$

While $\kappa_{e1} \rightarrow 1$ for strong electronic coupling (i.e. large H_{12}) such that $\nu_{e1} \gg \nu_n$, Eq (3) reduces to $\kappa_{e1} \approx \nu_{e1}/\nu_n$ for weaker coupling so that $\nu_{e1} \ll \nu_n$. For such "nonadiabatic" processes ($\kappa_{e1} \ll 1$), then, the combined preexponential factor $\kappa_{e1}\nu_n$ [Eq (2)] will become *independent* of the nuclear dynamics and proportional to H_{12}^2 ^{19a,24a} ("Golden Rule" limit). More sophisticated treatments of nonadiabatic effects have been developed.^{13,14c} A formalism has also been outlined that accounts for barrier-shape effects (via H_{12}) on the nuclear dynamics together with reaction nonadiabaticity and solvent inertial effects.^{24b} These treatments employ the conventional assumption that ΔG^* in the presence of substantial donor-acceptor orbital overlap is diminished by an amount equal to H_{12} (as in Fig. 1).^{8a,9c,25} A very recent quantum description of electronic coupling combined with solvent polarization predicts that the effect of H_{12} upon the barrier height can be

substantially smaller than this;³⁸ however, the corresponding influence upon the reaction adiabaticity (i.e. $\kappa_{e,1}$) typically differs only slightly from the conventional Landau-Zener predictions.³⁸

Illustrative Comparisons with Experiment:

(1) Rate-Solvent Friction Dependencies

The most common experimental tactic utilized so far to explore solvent dynamical effects in activated ET processes involves evaluating rate constants for electron exchange, k_{ex} , in a sequence of solvents selected so to yield suitable alterations in the dielectric friction and thereby in ν_n .¹⁵⁻¹⁸ Choosing symmetrical reactions (self exchange or electrochemical exchange) has the major virtue of eliminating solvent-dependent driving-force contributions to the free-energy barrier. After applying corrections for the solvent-dependent barrier height (vide infra), any remaining k_{ex} -solvent dependence can in principle be ascribed to variations in this dynamical term providing that K_p remains essentially constant [Eq. (2)]. The latter should be approximately the case, for example, for self-exchange reactions featuring weakly interacting solutes where one of the redox partners is uncharged.¹⁶ Alternatively, estimates of the preexponential factor $\kappa_{e,1}\nu_n$ can be obtained from k_{ob} and ΔG^* by using Eq. (2), and the dependence on τ_L^{-1} or other solvent dynamical parameters assessed (vide infra).^{15d,16a-c}

The form of the rate-solvent friction dependence is generally predicted from Eq (3) to be sensitive to the donor-acceptor electronic coupling. As an illustration of this point, Fig. 2 contains logarithmic plots of the calculated rate constant for a "model" self-exchange reaction, $k'_{ex}(\text{calc})$, in eleven solvents against τ_L^{-1} for a series of H_{12} values from 0.05 to 1.0 kcal mol⁻¹, as indicated. (The solvents, noted in the figure caption, each exhibit near-Debye dielectric behavior.) Details of these calculations are given in ref.

16d. Briefly, they refer to a $5.0 \text{ kcal mol}^{-1}$ barrier (for $H_{12} = 0$) for 3.8 \AA radius reactants (appropriate for metallocenes, *vide infra*). The bimolecular rate constants were extracted by means of a complete spatial integration of the "local unimolecular" values for the various reactant encounter geometries (i.e. different reactant internuclear distances) that contribute significantly to the observed ET rates.^{16d,24b} This procedure yields significantly smaller rate-friction dependencies than obtained from the simplified "preequilibrium" model;^{24b,39} the latter [Eq. (2)] presumes that only a narrow fixed range of precursor geometries (as denoted by K_p) contribute to k_{ex} .

The $\log k'_{ex}(\text{calc}) - \log \tau_L^{-1}$ dependencies in Fig. 2 are seen to be sensitive to the solvent friction (τ_L) as well as to the electronic coupling (H_{12}), the slopes increasing towards smaller τ_L^{-1} values and with increasing H_{12} . These trends can be understood qualitatively in terms of Eq. (3); enlarging H_{12} and/or τ_L will increase κ_{e1} and hence the degree to which solvent dynamics, rather than electron tunneling, controls the barrier-crossing frequency. (The scatter seen in Fig. 2 for some low-friction solvents is due to the variable influence of solvent inertial effects.^{16d,24b}) Significantly, the occurrence of substantial solvent friction effects upon the reaction rate is predicted to require the presence of relatively strong electronic coupling ($H_{12} \geq 0.2 \text{ kcal/mol}^{-1}$) for the typical range of τ_L values in Fig. 2. The additional presence of a substantial inner-shell component of the activation barrier is predicted to diminish further the rate-solvent friction dependence since the solvent dynamical influence on ν_n will necessarily be muted (*vide infra*).¹⁰

The strong sensitivity of the predicted rate-friction dependence to the electronic coupling seen in Fig. 2 suggests that information on the latter might be discernable from suitable solvent-dependent rate studies. In prac-

tice, the reliable extraction of such information, at least quantitatively, from solvent-dependent rate measurements is commonly thwarted by uncertainties in the data analysis, especially in the corrections for the solvent-dependent barrier height.^{15b,c,16a} An illuminating exception, however, is provided by some metallocene self-exchange reactions which have recently been examined in detail in our laboratory.^{16,40} These reactions involve redox couples of the form $\text{Cp}_2\text{M}^{+/0}$, where Cp = cyclopentadienyl and derivatives and M = Fe or Co. They have several virtues as solvent dynamical probes, including the presence of known small or negligible inner-shell barriers, sufficient solubility in a range of polar solvents, and suitability for self-exchange rate measurements by using proton NMR line-broadening. Most importantly, reliable estimates of the solvent-dependent barrier heights are available from measurements of optical electron-transfer energies, E_{op} , for related biferrocene cations.⁴⁰ (Under suitable conditions, $\Delta G_c^* = E_{op}/4$, where ΔG_c^* is the "cusp" barrier height, i.e. that referring to $\text{H}_{12} \rightarrow 0$).

Significantly, the k_{ex} values in a given solvent are sensitive to the metallocene structure, varying by factors up to ca. 100 fold.¹⁶ These rate differences have been traced primarily to variations in the donor-acceptor electronic coupling.^{16d,41} Although not evident initially,^{16a} a subsequent reevaluation of literature k_{ex} data for $\text{Cp}_2\text{Fe}^{+/0}$ ^{16b} together with further measurements yielded an interesting spectrum of rate-solvent friction behavior.^{16c} Pertinent results for five metallocene couples in eleven solvents (taken from ref. 16d) are summarized in Fig. 3, in the same format as the calculated rate-solvent friction plots in Fig. 2. The k'_{ex} values were obtained by correcting the experimental rate constants so to refer to a constant "cusp" barrier height of 5.0 kcal mol⁻¹ (the ΔG_c^* values vary only from ca. 4.6 to 5.4 kcal mol⁻¹).^{16d} The filled and open symbols in Fig. 3 refer to cobalt and iron metallocenes, respectively (see figure caption for

more details). Although some scatter is evident, these experimental results are closely reminiscent of the corresponding calculated traces (Fig. 2) in that the more facile reactions in a given solvent (i.e. those with larger H_{12}) display progressively greater dependencies of k'_{ex} upon τ_L^{-1} . Comparison of Fig. 3 with Fig. 2 enables approximate estimates of H_{12} for each reaction to be obtained: these vary from about 0.1 kcal mol⁻¹ for $Cp_2Fe^{+/0}$ (open triangles) to 0.5 kcal mol⁻¹ for $Cp_2Co^{+/0}$ (filled triangles) and 1.0 kcal mol⁻¹ for $Cp'_2Co^{+/0}$ (Cp' = pentamethylcyclopentadienyl; filled circles).

Interestingly, these H_{12} estimates are in approximate agreement with recent theoretical values obtained by Newton.⁴² The greater electronic coupling for the cobalt versus the iron metallocenes, in particular, can be understood qualitatively in terms of the ligand- and metal-centered nature of the molecular orbitals, respectively, that participate in electron transfer.⁴³ This finding, together with the reasonable internal consistency (within ca. 2-3 fold) observed between the absolute observed and calculated k'_{ex} values and the corresponding $\log k'_{ex}$ - $\log \tau_L^{-1}$ dependencies gives us confidence in the overall validity of the analysis. In particular, the results indicate that τ_L^{-1} can provide at least a semiquantitative description of the adiabatic barrier-crossing dynamics in Debye media.

Rate-solvent dependencies roughly consistent with this last conclusion have also been obtained for a number of other homogeneous-phase and electrochemical reactions.¹⁵⁻¹⁸ Thus the electrochemical exchange kinetics for $Cp_2Co^{+/0}$ and other metallocene redox couples yield uniformly solvent-dependent preexponential factors that correlate roughly with τ_L^{-1} in Debye solvents.^{15a-e} The derived $\kappa_{e1}\nu_n$ values for metallocene electrochemical exchange are insensitive to reactant structure and are comparable to those for the most facile metallocene self-exchange processes,^{16a} inferring that

the former follow uniformly adiabatic pathways.^{16c,41} Evidence for the occurrence of relatively *nonadiabatic* electrochemical pathways, however, has been obtained from a rate-solvent friction in another case, involving the large aliphatic couple tris(hexafluoroacetylacetonato)ruthenium(III)/(II).^{15f}

In the absence of experimental optical information on the solvent-dependent barriers, it is conventional to utilize ΔG^* estimates obtained from the Marcus and related dielectric continuum models. With due care, such procedures can at least provide a reliable diagnosis of solvent dynamical effects; i.e. the qualitative recognition of a solvent friction-dependent preexponential factor.^{15b,c,16a} An illustration of the limitations of this approach for *quantitative* rate-friction analyses, however, is provided by comparing optical electron-transfer energies for biferrocene cations with corresponding dielectric continuum predictions.⁴⁰ While the calculated barriers are largely within 10-20% of the measured values, these disparities depend systematically upon the magnitude of ΔG^* ; moreover, ΔG^* correlates roughly with τ_L^{-1} in common Debye solvents.^{15c,16b} These two factors can conspire to yield noticeably different inferred dependencies of $\kappa_{e1}\nu_n$ upon τ_L^{-1} depending if the experimental optical or the theoretical ΔG^* values are used for the analysis.^{16b} Interestingly, theoretical models of the reorganization energy that incorporate "solvent molecularity" effects, such as MSA and "nonlocal" electrostatic treatments, yield significantly improved agreement with the optical energies.^{40,45}

(2) Non-Debye Solvent Relaxation

Given the largely satisfactory picture noted above for metallocene self-exchange dynamics in Debye media, the examination of barrier-crossing frequencies in solvents featuring multiple relaxation times should provide an insightful test of the theoretical predictions noted above.^{16,25,50} To

this end, Table I compares inverse solvent relaxation times, τ_L^{-1} and τ_S^{-1} , obtained from dielectric loss and subpicosecond TDFS data, respectively (the latter from Barbara et al.^{2b,6a,49}), in eight solvents with preexponential factors $\kappa_{e1}\nu_n$ for a pair of metallocene self-exchange reactions. The $\kappa_{e1}\nu_n$ values were extracted from measured k_{ex} and ΔG^* values (see ref. 16c and footnotes for details). The redox couples $Cp_2^*Co^{+/0}$ (Cp^* = carboxymethylcyclopentadienyl) and $HMFc^{+/0}$ [hydroxymethyl(ferrocenium-ferrocene)] are chosen here since they display largely adiabatic and nonadiabatic behavior, respectively ($H_{12} \sim 0.5-1.0$ and 0.075 kcal mol⁻¹),^{16d} and can be examined in water as well as a range of nonaqueous solvents.^{16c} Two of the solvents, propylene carbonate and methanol, exhibit non-Debye dielectric behavior,^{46,48} also reflected in the pair of widely (ca 10 fold) differing τ_s values observed in both these media.⁶ Multiexponential TDFS decays are also seen for three other solvents in Table I.^{2b,6a,49} Note, however, the good agreement between τ_L and the average τ_s values for all six Debye solvents in Table I, even though the relaxation times vary by ca 20 fold.

The $\kappa_{e1}\nu_n$ values for $HMFc^{+/0}$ are uniformly smaller than τ_L^{-1} or τ_S^{-1} and roughly solvent independent, as expected for a largely nonadiabatic reaction (i.e. $\kappa_{e1} \ll 1$).^{16d} For $Cp_2^*Co^{+/0}$, however, the $\kappa_{e1}\nu_n$ values not only correlate well with the solvent relaxation dynamics, but are close to (within 1.5 fold of) the largest τ_S^{-1} value in all eight solvents. Although the agreement between the absolute $\kappa_{e1}\nu_n$ and τ_S^{-1} values seen in Table I is probably fortuitous given the inevitable uncertainties in extracting the former, the close correlation nonetheless demonstrates the importance of the more rapid solvent dynamical component in accelerating electron transfer. This finding is in broad agreement with the theoretical predictions noted above;^{9c,25,34-36} a more quantitative analysis yields solvent-dependent barrier-crossing

frequencies that are largely consistent with the predictions of the Hynes' model.⁵⁰

The results in methanol and water are perhaps of greatest interest.^{16c} The influence of the high-frequency relaxation component in the former media is particularly striking, yielding barrier-crossing frequencies that approach those in water and other low-friction media despite the presence of a markedly (10-30 fold) longer τ_L value. The physical origin of such rapid relaxation modes is unclear at present, although the high-frequency dielectric-loss component in primary alcohols has been ascribed to -OH group rotation.³⁰ Dipole translational relaxation may also contribute to the rapidity of the TDFS and barrier-crossing dynamics in methanol.^{16c,50}

Comparable results have also been obtained for other adiabatic metallo-cene reactions,^{15c,16e,25,50} although the presence of a rapid TDFS relaxation component is apparently not always reflected in accelerated ET dynamics.⁵⁰ Several factors may account for such observed differences.⁵⁰ For example, the presence of rapid dynamical components associated with local solvation ("solvent molecularity") effects are generally expected to be sensitive to the solute size and structure. The large polyaromatic solutes suitable for TDFS experiments may therefore engender significantly different dynamics than the ionic species commonly utilized in ET kinetics. Moreover, some differences are generally anticipated given that these measurements refer to the solvation dynamics of dipolar and ionic solutes, respectively.^{51,52}

Other Approaches and Future Prospects

While solvent-dependent rates for bimolecular electron exchange, especially self-exchange, reactions constitute the bulk of the experimental information on activated solvent dynamical effects gathered so far, other approaches could be used to some advantage. Examining the kinetics of unimolecular (preferably rigid intramolecular) electron-transfer to this

end would have the obvious virtue of eliminating uncertainties regarding the precursor-complex geometries and the energetics of their information. Few such studies aimed at elucidating solvent dynamical effects for activated ET have been reported so far, although as noted above there are a number of photoexcited intramolecular reactions examined that apparently feature small ($\leq k_B T$) barriers.^{2b,53}

Since τ_L is sensitive to temperature, T-dependent rate studies in a given medium should in some cases provide a useful means of diagnosing and examining solvent dynamical effects. This tactic has been utilized in several studies, again mostly involving small-barrier reactions.^{18d,54} This procedure in principle should be also useful for examining activated reactions. At least for bimolecular processes, however, the Arrhenius activation parameters can be affected greatly by intermolecular interactions.⁵⁵ Even for reactions involving monocharged cation/neutral pairs such as the metallocene self-exchanges considered above, unexpectedly low Arrhenius preexponential factors are usually obtained that probably reflect entropic contributions to the precursor complex stability.⁵⁶ This complication is absent for intramolecular electron transfer, so that valuable dynamical insight should be forthcoming from temperature-dependent studies of such activated processes in various solvents. It would be particularly desirable to examine sequences of such intramolecular systems having varying driving forces, in order to probe the dynamical consequences of varying the barrier height. Reliable information will be required, however, on the solvent- and temperature-dependent reaction thermodynamics in order to interpret fully the rate data.

A central issue, highlighted above, is the degree to which reaction adiabaticity is achieved, corresponding to rate control by solvent dynamics and other nuclear motion rather than by nonadiabatic electron hopping. The degree of electronic coupling that is evidently required to yield largely

adiabatic barrier crossing, at least in low-friction media at ambient temperatures ($H_{12} \geq 0.2 \text{ kcal mol}^{-1}$), restricts the chemical variety of outer-sphere ET processes liable to be controlled by solvent dynamics under these conditions to systems involving close approach of the reactant redox functionalities.

Solvent dynamical effects should often be prevalent, however, for inner-sphere ET and other "strong overlap" reactions, providing that the bond formation between the reaction centers also engenders sufficient donor-acceptor electronic coupling. While there is extensive theoretical work on some aspects of strong-overlap charge transfer,⁵⁷ corresponding experimental examinations of solvent-dependent dynamics are rare. One interesting recent example of the latter type, however, concerns the evaluation of primary kinetic isotope effects (k_H/k_D) for hydride transfer.⁵⁸ A significant solvent dependence of k_H/k_D was observed, from a maximum of ca 5-5.5 in low-friction to ca 3.0 in some other solvents. Although a simple relationship between k_H/k_D and solvent friction was not established, the results are roughly consistent with a shift from virtually complete rate control by hydride tunneling to partial control by solvent relaxation.⁵⁸ This interpretation is closely analogous to the phenomenon of solvent friction-dependent reaction adiabaticity for electron transfer, embodied in Figs. 2 and 3.

Along with the anticipated experimental developments, molecular dynamics simulations should play a significant future role in delineating solvent effects in activated ET and related processes.^{57,59} One hoped-for virtue of such simulations is that they should provide a common meeting ground between experimental results and relevant analytic theories of condensed-phase dynamics. As stressed above, the separation of energetic and dynamical factors remains a major stumbling block to the reliable interpretation of kinetic data in this vein. The concerted acquisition of parallel experimental

and simulation results, using realistic intermolecular models of the solute-solvent systems for the latter, could provide an insightful marriage for the future.

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His death in October 1989 tragically cut short a truly promising scientific career. George's abounding energy, enthusiasm, scholarship, intrepidity, humor, and love for science are qualities that will long be remembered by, and a continued inspiration for, all who knew "The Elf" (MJW).

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TABLE 1. Comparison between inverse solvent relaxation terms from dielectric loss and TDFS data with effective barrier-crossing frequencies for metallocene self exchanges.

Solvent	ΔG^* ^a kcal mol ⁻¹	τ_L^{-1} ^b ps ⁻¹	τ_S^{-1} ^c ps ⁻¹	$\kappa_{e1}\nu_n$, ps ⁻¹ ^d	
				Cp ₂ Co ^{+/0} ^e	HMFc ^{+/0} ^f
Acetonitrile	5.35	~2.5	1.8	2.5	0.2
Acetone	5.4	3.5	1.0 (53%) 3.5 (47%)	2	0.25
Nitromethane	5.3	4.5		3	0.4
Water	5.2	1.9	1.0 (50%) 4.0 (50%)	3.5 ^g	0.35 ^g
Benzonitrile	4.55	0.17	0.16 (61%) 0.47 (39%)	0.3	0.15
Nitrobenzene	4.55	0.19		0.15	0.12
Propylene Carbonate	5.25	(0.3)	0.24 (54%) 2.3 (46%)	1.5	
Methanol	5.2	(0.13)	0.10 (60%) 0.9 (40%)	1.5	0.45

^aCusp free-energy barrier for self-exchange reactions, estimated from optical electron-transfer energies for biferrocenylacetylene cation in indicated solvent (see refs. 16c,d, and 40 for details).

^bInverse longitudinal relaxation time for solvent indicated, obtained from dielectric loss spectra. See Table I of ref. 16d for data sources, except for propylene carbonate (from ref. 46) and for acetonitrile (from ref 47, assuming Debye behavior). Values for propylene carbonate and methanol given in parentheses since an additional higher-frequency dispersion is also evident in the dielectric loss spectra.^{46,48}

^cInverse solvation times, along with percentage weighting factors, obtained from TDFS data for the coumarin C152 (refs. 2b, 6a) except for water which refers to C343 (ref. 49)

^dEffective barrier-crossing frequency for metallocene self-exchange reaction indicated, obtained from experimental κ_{e1} values together with listed ΔG^* values, assuming that $K_p = 0.25 \text{ M}^{-1}$ [Eq(2)]. See ref 16c for kinetic data and other details; ΔG^* values for Cp₂Co^{+/0} taken to be 0.5 kcal mol⁻¹ smaller to allow for orbital overlap.^{16c}

^eCp₂Co^{+/0} = carboxymethyl (cobaltocenium-cobaltocene)[(CpCO₂Me)₂ Co^{+/0}]

^fHMFc^{+/0} = hydroxymethyl(ferrocenium-ferrocene)[Cp.CpCH₂OH)Fe^{+/0}]

^gRate data refers to D₂O.

Figure Captions

Fig. 1

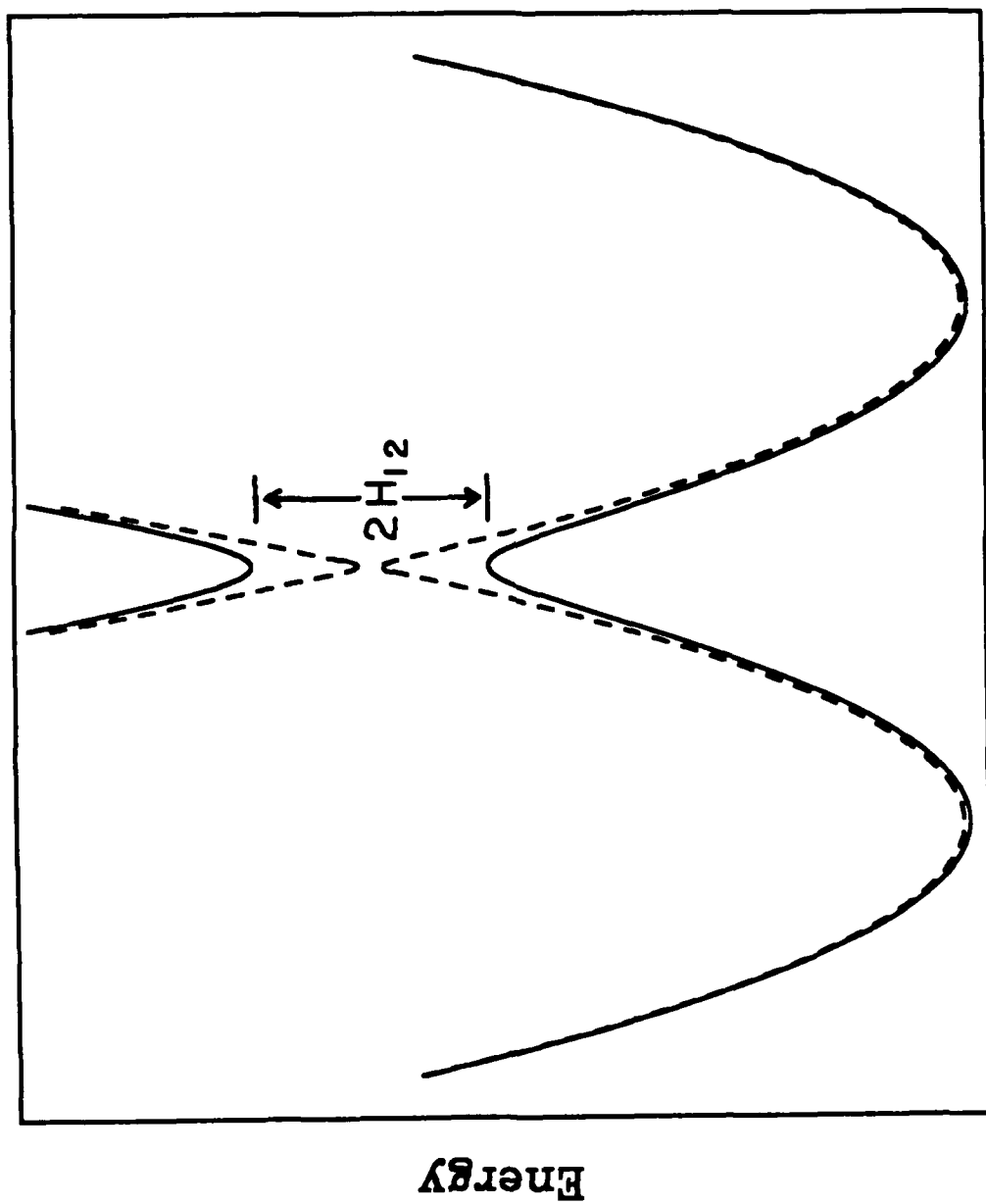
Schematic free energy-reaction coordinate profiles for symmetrical electron-transfer processes having small and large electronic matrix coupling elements, H_{12} (dashed and solid curves, respectively). From ref. 16d.

Fig. 2

Logarithmic plots of calculated "barrier-corrected" rate constants $M^{-1}s^{-1}$ (for 5.0 kcal mol⁻¹ "cusp" barrier), for electron self exchange versus inverse longitudinal relaxation time in eleven "Debye" solvents for the sequence of six electronic coupling matrix elements (at reactant contact) as indicated. See text and ref. 16d for details. Key to solvents: 1, acetonitrile; 2, propionitrile; 3, acetone; 4, D₂O; 5, nitromethane; 6, dimethylformamide; 7, dimethylsulfoxide; 8, benzonitrile; 9, nitrobenzene; 10, tetramethylurea; 11, hexamethylphosphoramide.

Fig. 3

Logarithmic plots of "barrier-corrected" rate constants (extracted from rate and optical barrier data) versus inverse longitudinal relaxation time for five metallocene self-exchange reactions in eleven solvents. See text and ref. 16d for further details, and Table I caption for key to solvents. Key to redox couples: filled circles, $Cp'_2Co^{+/0}$ (Cp' = pentamethylcyclopentadienyl); filled squares, $Cp^*_2Co^{+/0}$ (Cp^* = carboxymethylcyclopentadienyl); filled triangles, $Cp_2Co^{+/0}$; open triangles, $Cp_2Fe^{+/0}$; open squares, hydroxymethyl(ferrocenium-ferrocene).



Reaction Coordinate

FIG 1

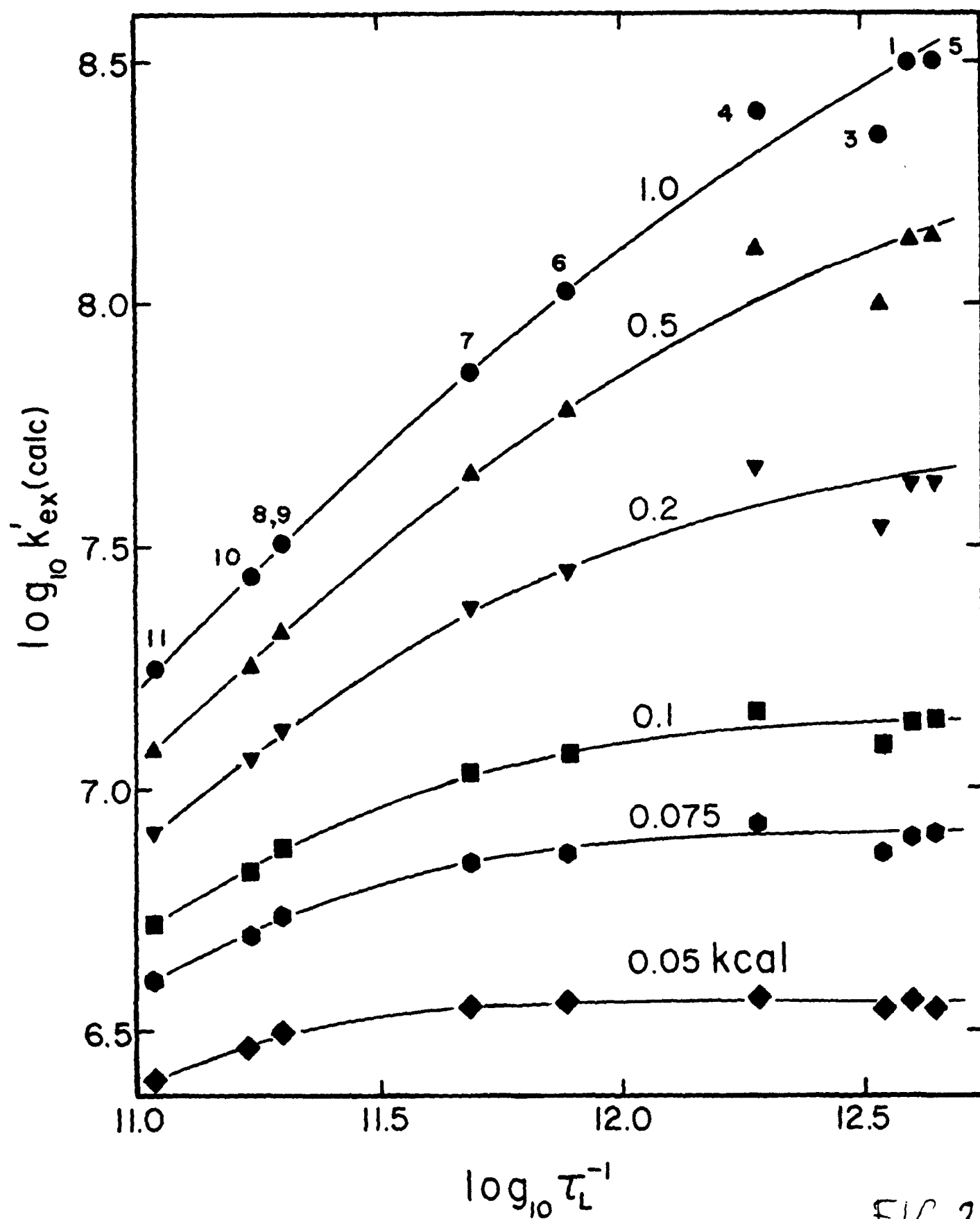


FIG 2

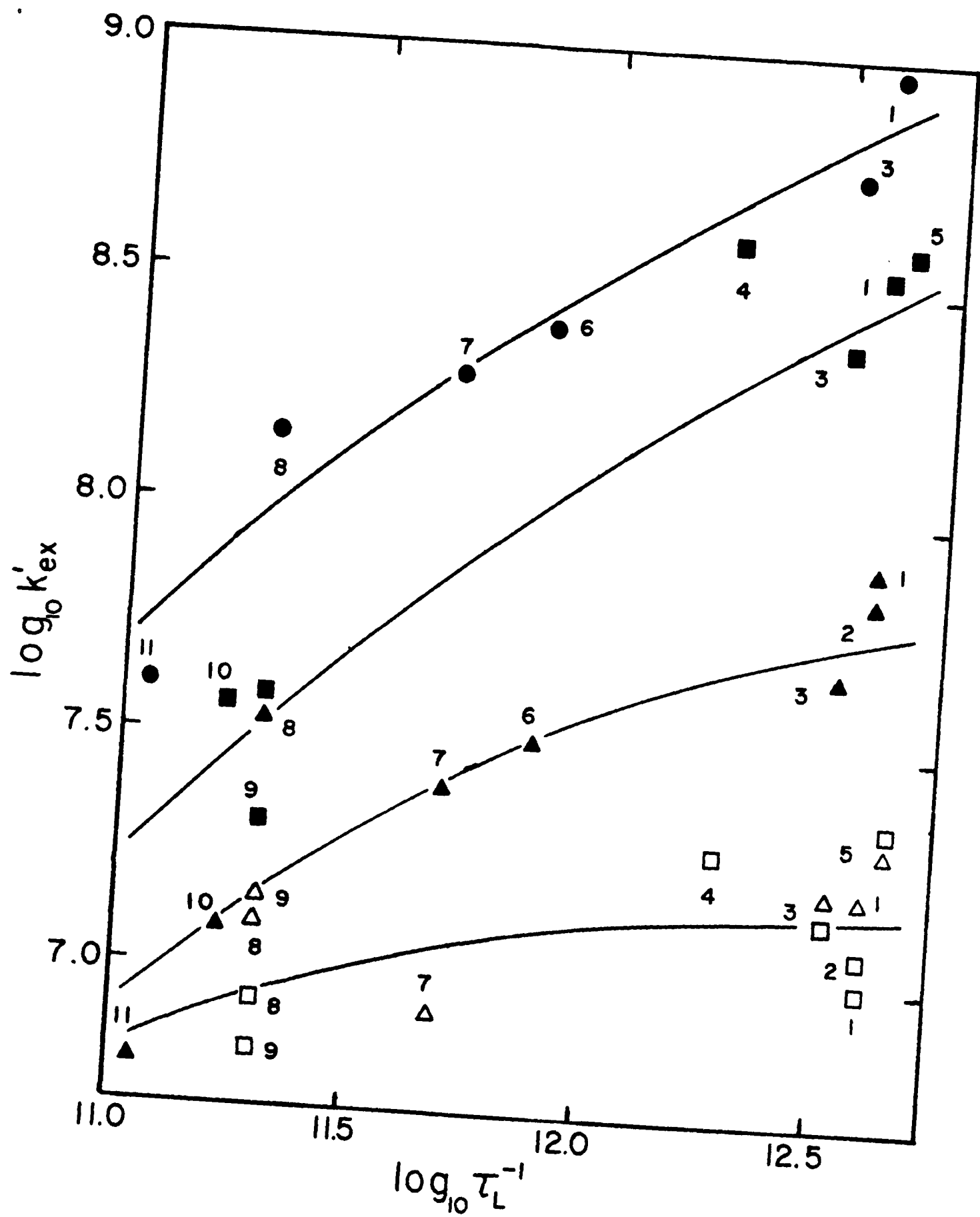


FIG 3